



Silicon semiconductor-assisted Brønsted acid-catalyzed dehydration: Highly selective synthesis of 5-hydroxymethylfurfural from fructose under visible light irradiation

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ABSTRACT

Semiconductor materials are used to promote Brønsted acid-catalyzed dehydration of fructose to 5-hydroxymethylfurfural (HMF) under visible light irradiation. In the proposed reaction system the semiconductors convert light to heat, transferring chemical energy to the substrates. We found that silicon was a more suitable semiconductor for the conversion of fructose to HMF compared with α -Fe₂O₃, WO₃, and TiO₂. Remarkably, a silicon semiconductor coated with silanol groups (Si-OH) affords HMF in almost quantitative yield (97%) even at 80 °C. This result suggests that the Si-OH catalyst provides energy selectively to the starting material fructose and not to desired product HMF, preventing side-reactions.

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1. Introduction

A huge amount of energy consumption in the world has been causing concerns about the fossil energy crisis and the climate change. In respond to these problems the efficient utilization of solar energy from sunlight has great potential because of its sustainable and clean characteristics. From this point of view, much attention has been paid to semiconductor materials as a photocatalyst converting light to chemical energy as an economical and environmentally friendly aid in organic synthesis [1]. To date, photocatalytic oxidation [2], reduction [3], C–H bond activation [4], C–C and C–N bond formation [5,6], and isomerization [7] have been achieved using photocatalysts. Semiconductors absorb supra bandgap photons to generate photoexcited electron (e^-) and hole (h^+) pairs in the conduction band (CB) and valence band (VB), respectively. The above-mentioned reactions are triggered by the photo-generated electron and/or hole or following generated radical species in such a photocatalytic system [1–8]. Therefore many investigators have been conducting research for the charge separated state upon photoexcitation including the photoinduced charge transfer.

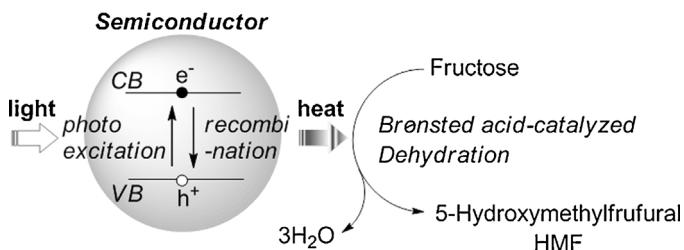
We study further application of semiconductors for organic reactions in order to contribute the development in synthetic

chemistry. Semiconductors harvest light and then photo-generated electron–hole recombination produces heat corresponding to the bandgap. From the consideration of this process a following semiconductor-assisted organic transformation system is proposed. The semiconductor introduced to the reaction system converts light into heat during photoexcitation and charge recombination, and then transfers heat to substrates. As a result, the activation energy for organic transformations can be supplied by a semiconductor. The conversion system of light to heat may reduce the energy consumption from the fossil as well as promote various organic reactions.

To test the hypothesis mentioned above, we focused on a Brønsted acid-catalyzed dehydration of fructose to 5-hydroxymethylfurfural (HMF). HMF has been widely recognized as one of the top bio-based platform chemicals of the future chemical industry: not only can it and its derivatives serve as fuels, but it can also replace oil-based building blocks in the production of polymers, the largest segment of the current chemical industry [9,10]. The most convenient synthetic method to produce HMF is based on the acid-catalyzed triple dehydration of fructose. Many types of acid catalysts have been used in this process, including mineral acids [11–13], organic acids [14], ion exchange resins [15], H-form zeolites [16], oxides [17], phosphates [18], heteropolyacids [19], and metal ions [20]. Traditional mineral acids possess the advantages of high reactivity, low cost and suitability for use in industrial processes [21–23]. However, mineral acids generally give low yield and selectivity of HMF because various

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Scheme 1. Semiconductor-assisted Brønsted acid-catalyzed dehydration of fructose to HMF.

bypyroducts are formed under the harsh reaction conditions required. Intermolecular reaction of HMF and/or partially dehydrated intermediates leads to condensation products, polymers and humins [12–15,21–25]. Formic and levulinic acids are the products of HMF rehydration over acidic catalysts [12–16,18–25].

It is generally recognized that inhibiting side reactions is very difficult at high temperature; for example, the reported syntheses of HMF [11–13,21–25]. In an attempt to overcome this problem, here we develop a new synthetic protocol with both high yield and selectivity for HMF even at low temperature. To achieve effective acid-catalyzed dehydration of fructose at low temperature, we introduce a heterogeneous semiconductor to the system to convert light to heat (Scheme 1). Here, we investigate the photocatalyst-assisted Brønsted acid-catalyzed dehydration of fructose to improve the synthesis of HMF, and elucidate a new entry of the semiconductor system into organic syntheses.

2. Experimental

2.1. Materials and reagents

D(–)-Fructose, 5-hydroxymethylfurfural (HMF), and levulinic and formic acids used as reactants and/or standard analysis agents were purchased from Wako Pure Chemical Industries, Ltd. Silicon (Si 99.999%; Aldrich), silicon (99%; Aldrich), α -iron(III) oxide (α -Fe₂O₃ 99.9%; Wako Pure Chemical Industries, Ltd.), tungsten(VI) oxide (WO₃; Aldrich), and titanium(IV) oxide, anatase form (TiO₂ 99.9%; Wako Pure Chemical Industries, Ltd.) were used as a semiconductor. Dispersions of Pd and Ru nanoparticles in divinylbenzene polymer (Wako Pure Chemical Industries, Ltd.) used as a metal source to prepare metal-supported Si semiconductors were purchased from Wako Pure Chemical Industries, Ltd. H₃PO₄, HCl, H₂SO₄, HCOOH, H₂O₂ (30%), and HF (46%) were purchased from Wako Pure Chemical Industries, Ltd. These commercially available reagents were used without further purification.

2.2. Preparation of 1 wt% Pd/Si and 1 wt% Ru/Si

Metal-supported semiconductors were prepared by an impregnation method. Silicon (99.999%) was used as a support. Si powder (2.0 g), deionized water (20 mL), and a calculated amount of metal nanoparticle (Pd or Ru) dispersion were mixed to give 1 wt% silicon after impregnation. The mixture was dried on a hot plate at 80 °C and then the resulting product was heat-treated under a stream of hydrogen gas at 150 °C for 1 h and 400 °C for 15 min. The sample was rinsed three times with acetone, and then dried at 80 °C. The content of noble metals in the samples was estimated to be 1 wt% according to the amount of precursor used.

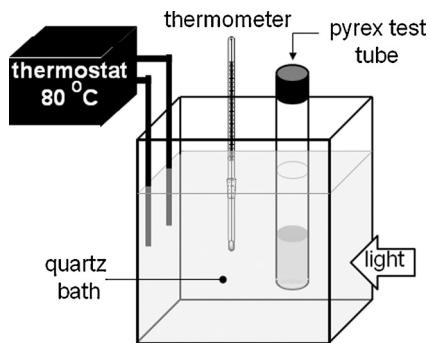


Fig. 1. Schematic diagram of the photoirradiation reaction system.

2.3. Preparation of silicon semiconductor coated with silanol groups (Si-OH)

Silicon (99%) was used as a starting material. Si powder (2 g) was stirred in aqueous HF (46%, 40 mL) for 40 min. The sample was rinsed three times with deionized water, twice with methanol and acetone, and then dried under atmospheric conditions for 24 h. The obtained powder (1.6 g) was added to aqueous H₂O₂ (30%, 20 mL) and stirred for 24 h. The solid residue was washed with deionized water three times and acetone twice. The resulting solid was dried under vacuum at room temperature.

The BET surface areas of samples were measured by nitrogen adsorption at –196 °C (BELSORP-miniII, BEL Japan, Inc.). Prior to nitrogen physisorption, the samples were degassed under vacuum at 200 °C for 2 h.

The X-ray diffraction (XRD) measurements were carried out on a Rigaku RINT 2100/Ui X-ray diffractometer scanning from 20° to 80° (2 θ) at a rate 2° min^{–1} using Cu K α radiation (λ = 0.15418 nm) source. The applied voltage and current were 40 kV and 20 mA, respectively.

The total acid capacity of Si-OH was determined by titration with NaOH. 50.0 mg of Si-OH was added to a 1.0 × 10^{–1} M NaCl solution after an initial pH measurement was recorded. Then, a 2.0 × 10^{–4} M NaOH solution was titrated into the stirred solution until the initial pH was achieved. The NaOH amount required in this titration was used to calculate the total number of silanol groups.

2.4. Brønsted acid-catalyzed conversion of fructose in the presence of semiconductor

A suspension of fructose (10–40 mg), mineral acid (1.2–6.9 M) and semiconductor powder (40 mg) in H₂O or DMSO/H₂O (1:1) (4.4 or 4.0 mL) was placed in a Pyrex test tube (14.5 mm inner diameter (I.D.) × 16.5 mm outer diameter). The test tube was positioned in a quartz bath and the temperature of the bath was controlled at 80 °C with a thermostat (Fig. 1). The suspension was stirred and photoirradiation was carried out through a UV-cut off filter (SC0750, Asahi Spectra Co., Ltd) using a Xe lamp (300 W, LX-300F, PE ILS) as the light source. After 5 h, the resulting mixture was filtered to remove the insoluble powder.

The resultant aqueous solution was analyzed with two high-performance liquid chromatography (HPLC) systems to investigate the contents of organic acids and sugars. Analytical HPLC for organic acid analysis was carried out using a Shimadzu CTO-20AC column oven, LC-20AD pump, SPD-M20A UV/vis detector for HMF, and RID-10A detector for formic and levulinic acids. Separations were performed on an Ultron PS-80H column (8.0 mm I.D. × 300 mm length, Shinwa Chemical Industries, Ltd.) at 50 °C using aqueous HClO₄ (pH 2.1) as the mobile phase (1.0 mL/min). The quantitative measurement of fructose by HPLC used a post-column fluorescence detection method with arginine as the reagent. The reducing

Table 1Effect of semiconductor on the dehydration of fructose.^a

Entry	Semiconductor	Fructose conversion ^b (%)	HMF yield ^{b,c} (%)
1	Si	25	16 (62)
2	α -Fe ₂ O ₃	26	6 (25)
3	WO ₃	25	5 (20)
4 ^d	TiO ₂	99	0 (0)
5	–	10	4 (40)
6 ^e	Si	17	9 (53)

^a Reaction conditions: fructose (40 mg), aq. H₃PO₄ (1.2 M, 4.4 mL), semiconductor (40 mg), photoirradiation with a xenon lamp through a UV cut-off filter (375 nm < λ < 800 nm), bath temperature = 80 °C, time = 5 h.

^b Determined by HPLC analysis.

^c Selectivity for HMF is given in parentheses.

^d Photoirradiation with a xenon lamp without a UV cut-off filter.

^e No photoirradiation.

Sugar analysis system was equipped with a Shimadzu CTO-20AC column oven, two LC-20AD pumps, RF-20A fluorescence detector, and Ultron PS-80H column (8.0 mm I.D. × 300 mm length, Shinwa Chemical Industries, Ltd.). Separations were performed on a Shodex Asahipak NH2P-50 4E column (4.6 mm I.D. × 250 mm length, Showa Denko K. K.) with a Shodex Asahipak NH2P-50 4A guard column (4.6 mm I.D. × 10 mm length, Showa Denko K. K.) at 45 °C using H₂O/CH₃CN/85% H₃PO₄ (= 15:85:0.3) as the mobile phase (0.8 mL/min). Reactions were performed in a chemical reaction box (CRB-6A) using a mixture of boric acid/potassium borate buffer (pH 9.3) and aqueous arginine as a reagent at a flow rate of 0.5 mL/min at 150 °C.

In some cases the yield of HMF was monitored by UV-vis spectroscopic analysis [26]. UV spectra were measured with a Shimadzu UV-1800 spectrophotometer. The concentration of HMF was estimated from its absorbance at 284 nm.

In the cases using DMSO/H₂O as a solvent, the products were extracted with diethyl ether prior to GC analysis. Analytical GC was carried out using a Shimadzu GC-2014 GC with an Inert CAP 1 column (0.25 mm I.D. × 60 m length, GL Sciences).

3. Results and discussion

3.1. Semiconductor-assisted Brønsted acid-catalyzed dehydration of fructose

3.1.1. Effect of semiconductor on dehydration of fructose using H₃PO₄

First, a number of semiconductor powders were screened (Si, α -Fe₂O₃, WO₃, and TiO₂) to determine the preferred semiconductor for further studies. Screening experiments were conducted by heating fructose **1** (40.0 mg) and a semiconductor powder (40.0 mg) in aqueous H₃PO₄ (1.2 M, 4.4 mL) at 80 °C for 5 h (Scheme 2). The reaction was irradiated with visible light (375 nm < λ < 800 nm) from a xenon lamp through a UV cut-off filter. When testing UV-active TiO₂, the reaction was conducted under irradiation with UV light from a xenon lamp without a UV cut-off filter. The conversion of fructose was increased in the presence of semiconductors even at 80 °C (Table 1, entries 1–4). Even in the presence of silicon, the conversion decreased under dark condition (Table 1, entry 6). Hence, semiconductors may transfer chemical energy to substrates by converting light to heat. The obtained yields and selectivities for HMF 2 indicated that Si was best semiconductor for the dehydration of fructose to produce HMF (Table 1, entry 1). Although TiO₂ converted fructose quantitatively, no HMF was observed. Absorption of a photon by TiO₂ generates a reactive electron–hole pair, so photoexcited TiO₂ can oxidatively decompose most organic substrates including the starting material, fructose, and the desired product, HMF [27]. The oxidation potential of Si is more positive than those of the other semiconductors, so it is unable to abstract electrons fructose and

Table 2Effect of acid catalyst.^a

Entry	Acid catalyst	Fructose conversion ^b (%)	HMF yield ^{b,c} (%)
1	H ₃ PO ₄	44	23 (52)
2	HCl	100	0.7 (0.7)
3	H ₂ SO ₄	99	0.7 (0.7)
4	HCOOH	2.3	1.9 (83)

^a Reaction conditions: fructose (40 mg), acid solution (2.3 M, 4.4 mL), Si (40 mg), photoirradiation with a xenon lamp through a UV cut-off filter (375 nm < λ < 800 nm), bath temperature = 80 °C, reaction time = 5 h.

^b Determined by HPLC analysis.

^c Selectivity for HMF is given in parentheses.

HMF [28]. Si is well known as one of the best materials for solar energy conversion because of its narrow band-gap.

3.1.2. Effect of acid catalyst on the Si semiconductor-assisted dehydration of fructose

The yield and selectivity for HMF during fructose conversion also depend on the catalyst acidity. Table 2 shows the conversion of fructose and selectivity for HMF in the presence of Si semiconductor using different acid catalysts. In the case of H₃PO₄, HMF was generated with moderate yield and selectivity (Table 2, entry 1). HCl and H₂SO₄ converted fructose almost quantitatively, but only a small amount of HMF formed (Table 2, entries 2 and 3, respectively). These results indicate that further decompositions may take place using strong acids under these conditions. In contrast, the weak acid HCOOH provided HMF with good selectivity but low fructose conversion (Table 2, entry 4). The pioneering work of photocatalytic hydrogen evolution using platinum-loaded silicon indicated that HCOOH was the most efficient sacrificial reagent for this reaction [29]. Therefore, the dehydration of fructose and decomposition of HCOOH might compete in the present reaction.

When transition metal-loaded silicon, 1 wt% Pd/Si and 1 wt% Ru/Si, were added to the reaction of fructose under similar conditions, no HMF was generated. The loaded transition metal traps photoexcited electrons to achieve electron–hole recombination. The reductive and oxidative decomposition of HCOOH by electrons and holes then produces hydrogen and carbon dioxide, respectively. These processes can inhibit the conversion of light into heat during charge recombination on the Si phase. In addition, Si is inactive, especially for oxidation of H₃PO₄, when the decomposition voltage of H₃PO₄ is considered. It was concluded that the yield of HMF was affected by the conversion of light to heat.

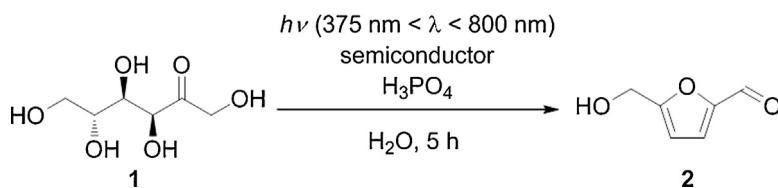
3.1.3. Effect of concentrations of H₃PO₄ and fructose on the Si-assisted dehydration of fructose

A number of experiments were conducted to optimize the concentrations of H₃PO₄ and fructose (Table 3). The comparison of the H₃PO₄ concentrations ranging from 0.23 M to 9.2 M suggested that the optimum H₃PO₄ concentration was 4.6 M (Table 3, entries 1–6). Moreover decreasing the initial amount of fructose increased the yield of HMF, which may be caused by suppression of the condensation reaction of HMF and/or reaction intermediates at low concentration (Table 3, entries 4 and 7–9). Further prolonging the reaction time under the same reaction conditions decreased the yield of HMF because of its decomposition to formic and levulinic acids.

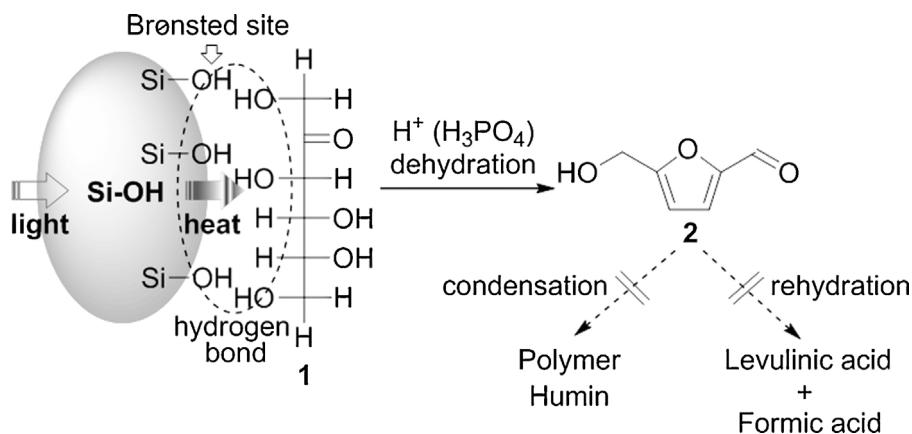
3.2. Highly selective synthesis of HMF using Si-OH semiconductor under visible-light irradiation

3.2.1. Selective promoting of dehydration of fructose to HMF using Si-OH semiconductor

Although Si-assisted acid-catalyzed dehydration of fructose gave HMF even at 80 °C, the yield was moderate because of



Scheme 2. Brønsted acid-catalyzed dehydration of fructose to HMF in the presence of semiconductor.



Scheme 3. Mechanistic design of selective promoting of acid-catalyzed dehydration of fructose to HMF using Si-OH.

sequential side reactions; hydrolysis and/or condensation of HMF. In particular, water as a reaction medium promotes rehydration of HMF, resulting in the formation of acids and polymeric products [30]. Thus, the removal of HMF or water from the aqueous reaction mixture has been conducted to suppress these undesired side reactions, increasing the selectivity for HMF. Dumesic and Román-Leshkov proposed a two phase reactor system to separate HMF from aqueous reaction media [31]. Continuous extraction of HMF into the organic phase in a biphasic reaction system increased selectivity for HMF by inhibiting further reactions [22,31–33]. Shimizu reported that removing water from the reaction mixture by mild evacuation resulted in high selectivity for the hydration of fructose over solid acid catalysts in organic solvents [34]. However these methods need the continuous extraction or the evacuation apparatus in the reaction system.

The overall conversion of fructose including dehydration, hydrolysis and condensation may be a downhill reaction [35]. It is generally recognized to be very difficult to control such sequential reactions especially under high reaction temperature. In addition, dehydration and rehydration can both be acid catalyzed and have

very similar activation energies [35,36], making selective synthesis of HMF difficult. This is a serious problem in HMF production [11–25]. As mentioned above, the chemical energy for the acid-catalyzed reactions can be provided by using a semiconductor to convert light to heat. Moreover, use of this semiconductor system to selectively heat fructose can assist HMF synthesis and prevent further side-reactions. To further improve this reaction protocol, we designed a silicon semiconductor coated with silanol groups (Si-OH). If fructose is adsorbed selectively on the silicon surface by hydrogen bonding between hydroxyl groups of fructose and silanol groups of the silicon surface, chemical energy might be transferred effectively to fructose from Si. H_3PO_4 is used as a suitable Brønsted acid-catalyst for the dehydration of fructose. In addition Si-OH might act as a Brønsted acid. In this system, fructose should be selectively activated on the Si surface and then converted to HMF. HMF is less polar than fructose, so it may be released from the hydrophilic silicon surface. This should prevent HMF from receiving additional heating, stopping it from undergoing further reactions, such as rehydration and condensation (Scheme 3).

3.2.2. Synthesis of Si-OH semiconductor

Si-OH semiconductor was prepared as follows. Si was washed with aqueous HF to remove SiO_2 on the silicon surface, and then Si was functionalized with silanol groups by oxidation with H_2O_2 (Scheme 4). Although the former dehydration experiments used highly pure Si (99.999%), the Si-OH semiconductor was synthesized with less pure Si (99%). The less pure Si contains more impurities or surface defects, which facilitate electron–hole recombination, making it suitable as a semiconductor for the synthesis of HMF.

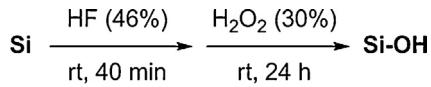
The BET surface area of starting material Si (99%) increased after the treatment with HF based on the removal of SiO_2 on the Si surface (Si (99%); $1.00 \text{ m}^2/\text{g}$, HF-treated Si; $1.88 \text{ m}^2/\text{g}$). The synthesized

Table 3
Effect of concentrations of H_3PO_4 and fructose.^a

Entry	H_3PO_4 (M)	Fructose (mg)	HMF yield ^b (%)
1	0.23	40	1.9
2	0.46	40	3.7
3	2.3	40	23
4	4.6	40	40
5	6.9	40	23
6	9.2	40	8.3
7	4.6	20	42
8	4.6	10	57
9	4.6	4.0	46

^a Reaction conditions: acid solution (4.4 mL), Si (40 mg), photoirradiation with a xenon lamp through a UV cut-off filter (375 nm < λ < 800 nm), bath temperature = 80 °C, reaction time = 5 h.

^b Determined by UV-vis spectroscopy monitoring at 284 nm. UV spectra can be used as a rapid and convenient method to estimate the amount of HMF in aqueous acids, see Ref. [26].



Scheme 4. Synthesis of Si-OH Semiconductor.

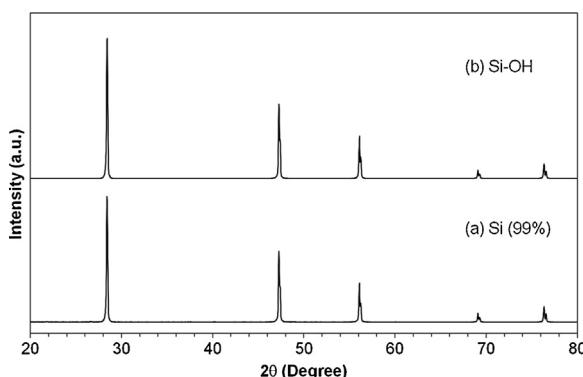
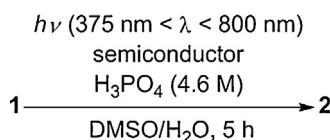


Fig. 2. XRD patterns for Si (99%) (a) and Si-OH (b).



Scheme 5. Selective synthesis of HMF using semiconductor under visible-light irradiation.

Si-OH catalyst showed the smaller BET surface area of 1.28 m²/g than the HF-treated Si. It may be considered that the oxidation treatment to coat on the Si-OH surface with silanol groups reduces the BET surface area. The number of acid sites of Si-OH, as determined by titration, was 2.2 μ mol/g, which may be in agreement with the number of silanol groups introduced on the silicon surface. The X-ray powder diffractogram shows clearly that Si-OH has the crystalline of silicon (Fig. 2). Hence the crystalline structure is stable on the course of Si-OH preparation.

3.2.3. Si-OH-assisted Brønsted acid-catalyzed dehydration of fructose

Acid-catalyzed reactions of fructose **1** were carried out in DMSO/H₂O using the prepared Si-OH semiconductor under visible light irradiation at 80 °C (Scheme 5). A mixture of DMSO and H₂O was used as the reaction solvent because it increased the selective absorption/desorption character of Si-OH compared with H₂O only. Similarly, reactions using both high and low purity Si were examined to compare their properties. Si (99%) afforded HMF **2** in better yield than Si (99.999%) (Table 4, entries 1 and 2, respectively). This is because the distance between charge recombination centers should be smaller in low purity Si than in high purity Si and, therefore, charge recombination may become fast enough to give the desired conversion of light to heat. Using Si-OH dramatically increased the yield of HMF up to 97% (Table 4, entry 3). To clarify

the effect of photoirradiation, the same reaction was conducted in the dark, which decreased the yield of HMF (Table 4, entry 4). As expected, visible light-activated Si-OH can produce chemical energy to promote the acid-catalyzed dehydration of fructose. The pH values indicated the strong acidity of the reaction solution, so they were kept after the reaction. Si-OH gave HMF in better yield even in the dark than Si, which indicated that Si-OH could play a role as a Brønsted acid-catalyst [37]. In addition, Si-OH can selectively absorb and activate fructose to facilitate its conversion to HMF. HMF is stable during the course of the reaction because it is desorbed from the Si-OH surface. This allows reaction system using Si-OH to promote the dehydration of fructose and suppress side reactions such as rehydration and condensation of HMF as shown in Scheme 3.

4. Conclusions

We found that semiconductors assisted the Brønsted acid-catalyzed dehydration of fructose through the conversion of light to heat. In particular, visible light-activated Si-OH semiconductor prevents undesired side-reactions to give HMF from fructose almost quantitatively at 80 °C. This result was achieved because of the molecular recognition ability of Si-OH to selectively adsorb (desorb) fructose (HMF). This is the first use of a semiconductor system in organic transformation. This basic concept using semiconductors, in particular, visible light-activated silicon, will contribute to the development of semiconductor materials capable of promoting not only conversions of sugars to provide valuable chemicals but also a wide variety of organic synthetic reactions, especially to achieve control of sequential reactions.

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Table 4
Si-OH semiconductor-assisted Brønsted acid-catalyzed dehydration of fructose.^a

Entry	Semiconductor	HMF yield ^b (%)	pH value ^c	
			Before reaction	After reaction
1	Si (99.999%)	45	0.47	0.43
2	Si (99%)	59	0.48	0.43
3	Si-OH	97	0.48	0.46
4 ^d	Si-OH	63	0.48	0.47

^a Reaction conditions: fructose (10 mg), H_3PO_4 (4.6 M) in 4.0 mL of DMSO/H₂O (=1:1), semiconductor (40 mg), photoirradiation with a xenon lamp through a UV-cut off filter (375 nm < λ < 800 nm), bath temperature = 80 °C, time = 5 h.

^b Determined by GC analysis.

^c pH values of the reaction solution.

^d No photoirradiation.

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